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SOLUBILITY OF HELIUM AND ARGON IN LIQUID SODIUM

E. Veleckis, S. K. Dhar,
F. A. Cafasso, and H. M. Feder

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Chemical Engineering Division

April 1971

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ABSTRACT

The solubilities of helium and argon in liquid sodium were determined as functions of pressure and temperature. The data obeyed Henry's law to at least 9 atm. In the temperature range 330–550°C, the solubilities may be represented by the following linear equations: helium, $\log \lambda = 0.516 - 3078T^{-1}$; argon, $\log \lambda = 1.08 - 4462T^{-1}$; where λ is the Ostwald coefficient. The 95% confidence limits of the mean value of λ predicted by these equations are ±4% for helium and ±16% for argon. For the standard state defined as one gram-atom of ideal gas confined to a volume equal to the molar volume of sodium, the heats of solution are 14.1 ± 0.6 kcal/mol for helium and 20.4 ± 2.1 kcal/mol for argon. The results are compared with experimental data of others and with calculations based on existing theoretical models.

INTRODUCTION

The thermodynamics of alloy formation is sufficiently complex that especially simple binary systems are desirable objects of theoretical and experimental study. The noble gases presumably dissolve in liquid metals as neutral atoms; if so, the polarization of the dissolved atoms by the fluctuating fields of the solvent should be the only source of attractive interactions. The electronic structures of the alkali metals are better understood than those of other metals; hence the use of the alkali metals as solvents for the noble gases should simplify the evaluation of these polarization forces. The alkali metal-noble gas solutions, therefore, constitute a class of especially simple binary alloys worthy of study. Measurement of the solubilities of noble gases in liquid alkali metals affords a convenient method of evaluating the thermodynamics of alloy formation.

Measurements of the solubility of noble gases in liquid metals, or theoretical discussions thereof, are sparse. Epstein [1] calculated the solubility of helium in sodium using Hildebrand's solubility parameters. McMillan [2] predicted the solubility of xenon in liquid bismuth, which was subsequently measured by Eshaya and Kenney [3], Mitra [4], and Hewitt, Lacey and Lyall [5]. Johnson and Shuttleworth [6] and Johnson [7] measured the solubility of krypton in liquid Pb, Sn, Ag, Cd, and In and attempted to rationalize their results. The only data reported on the solubility of noble gases in liquid alkali metals are those by Mitra [4], who measured the solubility of xenon in sodium; by Slotnick, Kapelner, and Cleary [8], who measured the solubility of helium in liquid lithium and potassium; and by Thormeier [9], who measured the solubility of helium and argon in liquid sodium concurrently with the present study. Except for an inconclusive test in the Li-He system [8], the validity of Henry's law had not been examined for noble gas-metal systems prior to this work. Departures from Henry's law at moderate pressures were not expected; however, to support the presumption of a solution as single, neutral atoms, a conclusive test of Henry's law was deemed necessary.

In the present work, attention was focused on the temperature and pressure variations of the solubility of helium and argon in liquid sodium. These systems were of interest for the reasons already given; in addition, helium and argon are generally used as cover gases in liquid-sodium-cooled nuclear reactors, and information on their solubilities in sodium is needed by reactor designers.

EXPERIMENTAL SECTION

The equilibration and separation technique used was adapted from Grimes, Smith, and Watson [10], who had applied it to the determination of the solubility of noble gases in fused salts. In the present work, liquid sodium was saturated with the gas whose solubility was to be measured at a preselected temperature and pressure. The saturated sodium was transferred to another container, where the solution was stripped of the dissolved species by sparging. The desired component of the resulting gas mixture was concentrated by selective adsorption and quantitatively assayed. This procedure incorporates special features which assure adequate equilibration, complete separation, and quantitative analysis, even though the expected gas solubilities are very small. These features include (1) means for removing suspended solid particles (which may capture small bubbles) from the liquid to be saturated, (2) prolonged bubbling of the saturating gas through the liquid, (3) a prolonged quiescent period to promote the coalescence and escape of gas bubbles, (4) very slow transfer of a portion of the saturated liquid via a bottom outlet to avoid the inclusion of liquid from the vicinity of certain surfaces,* (5) a prolonged sparging period to promote the stripping of the dissolved species, and (6) a procedure for distinguishing the stripped gas from extraneous sources of the same material.

APPARATUS

Figure 1 is a schematic diagram of the apparatus used. Three cylindrical vessels (4-1/2-in. diameter, 16 in. high) fabricated from Type 316 stainless steel were interconnected by heated 1/4-in. sodium transfer lines equipped with needle valves. In vessel A ("purifier"), filtration was carried out periodically as a precaution against the accumulation of solid sodium oxide particles from air inleakage. Saturating gas was bubbled through the liquid contained in vessel B ("saturator") via a coiled tube with sixty 3/16-in. perforations directed toward the bottom of the vessel. In vessel C ("stripper"), the stripping gas was introduced through a Micro Metallic Corp. 10-cm stainless steel dispersion disc having a 5-μ mean pore size. The volume of sodium in this vessel was calculated from its geometry and the sodium level. The level was measured to the nearest 0.5 cm with a Mine Safety Appliances Corp. liquid-level probe.

The three vessels were heated with 20-in.-high Marshall Products Co. split-type electric furnaces. Temperature was measured in each vessel with a Chromel-Alumel thermocouple in a thermowell.

Separate gas-circulation loops made of 1/4-in. Type 304 stainless steel tubing were connected to the saturator and to the stripper. Each loop contained a diaphragm pump (Lapp Pulsafeeder, Model CP-1) designed for pressures up to 15 atm, a flowmeter (Hastings Mass Flowmeter, Model LF), and a Bourdon pressure gauge. Air-cooled condensers located just above each vessel prevented sodium vapor from entering the gas-circulation systems. The condensers were periodically heated to free them of sodium. In these loops, all valves exposed to sodium had Stellite seats; those in less critical positions had Teflon seats.

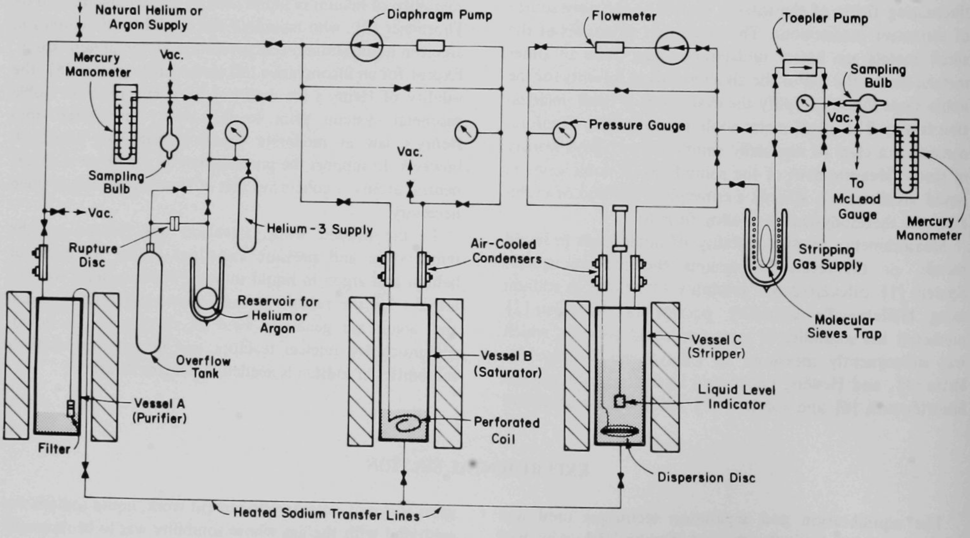
Natural Helium or Argon Supply
Diaphragm Pump
Flowmeter
Toepler Pump
Mercury Manometer
Vac.
Sampling Bulb
Sampling Bulb
Vac.
Pressure Gauge
Vac.
Vac.
To McLeod Gauge
Mercury Manometer
Vac.
Helium - 3 Supply
Rupture Disc
Air-Cooled Condensers
Stripping Gas Supply
Reservoir for Helium or Argon
Molecular Sieves Trap
Overflow Tank
Vessel B (Saturator)
Vessel C (Stripper)
Vessel A (Purifier)
Liquid Level Indicator
Filter
Perforated Coil
Dispersion Disc
Heated Sodium Transfer Lines

Fig. 1. Schematic Diagram of Gas Solubility Apparatus. ANL Neg. No. 308-2319.

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*The sodium-gas interfaces may be enriched in the saturating gas by adsorption. (See Refs. 3, 6, and 7.)

MATERIALS

Helium-3 (99.5%) was purchased from the Mound Laboratory, Miamisburg, Ohio, and ultrahigh-purity (99.999%) natural helium from the Matheson Company; an isotopic mixture of these (~30% ^{3}He) was prepared by condensing appropriate amounts of each on activated charcoal (Barnebey-Cheney Type 513) cooled to 4°K. Ultrahigh-purity (99.999%) argon was purchased from the Matheson Company; it contained no detectable helium. Reactor-grade sodium was purified in situ by periodic transfers of sodium (heated to 500°C) to the purifier, where it was cooled to 150°C and passed through a porous metal filter to remove insolubles. At 150°C the solubility of oxygen (the main impurity) is ~2 ppm [11].

PROCEDURE FOR HELIUM

Approximately 2.5 liters of liquid sodium in the saturator was heated to and maintained at the desired temperature, and the isotopic helium mixture was pumped through it at a rate of 1 liter/min for 2 hr. Pumping was then stopped, and the sodium was left undisturbed overnight. Throughout this period, the saturator temperature was maintained constant and the pressure (predetermined by the quantity of gas in the saturator loop) was measured. The needle valves in the sodium transfer line between the saturator and stripper were then slightly opened until ~2 liters of sodium were transferred into the closed, evacuated stripper. During this period of ~5 min, the helium pressure in the saturator was maintained at its initial value by the admission of additional isotopic helium mixture. The sodium in the stripper was cooled to ~130°C and stripped of the dissolved helium by continuously pumping 1 liter of argon at atmospheric pressure through the dispersion disc at 750 cm^3/min for 2 hr. When the stripping was complete, the volume of sodium that had been transferred was measured.

The gas mixture in the stripper loop generally contained 0.01 to 0.15% helium. To enhance the accuracy of analysis, it was desirable to concentrate the helium. This was done by Toepler-pumping the mixture through liquid-nitrogen-cooled Molecular Sieves (Linde Company Type 5A) into a sampling bulb of known volume. In this process, the argon was nearly quantitatively and selectively retained on the Sieves, and the final helium concentration was at least 95%. Tests of the recovery procedure with known quantities of helium indicated that recovery of 0.4 cm^3-atm or more was nearly quantitative. With smaller quantities, recoveries decreased; e.g., with 0.04 cm^3-atm, the recovery was 65%. A calibration curve of percent recovery versus quantity of helium was obtained and applied to the analytical data.

The concentration of the helium isotopes was determined by mass spectrometry. The function of the added ^{3}He was to distinguish between the helium obtained on exsolution from sodium and any tramp (^{4}He) helium. Any decrease in the ^{3}He relative concentration would have been attributed to dilution by natural helium, and an appropriate correction would have been made; no such correction was ever necessary.

PROCEDURE FOR ARGON

Natural argon was the solute gas, and helium was used for sparging. The resulting helium-argon mixture contained from 5×10^{-4} to 2×10^{-2}% argon. The argon concentration was increased by pumping the mixture through a controlled leak into a liquid-nitrogen-cooled Molecular Sieves Type 5A trap. The trap was heated to 300°C, and a measured portion of the desorbed gas was assayed for argon. The assayed samples contained from 4×10^{-2} to 3% argon, ~0.1% nitrogen, the balance being helium. Tests of this procedure with argon-helium mixtures of known compositions showed that, within experimental uncertainties, a quantitative recovery of argon was achieved.

The gas analyses were made with a gas chromatograph designed for an adequate separation of argon and nitrogen. The column was made of 8-ft-long, 1/4-in. dia stainless steel tubing packed with Molecular Sieves Type 5A, operated at 0°C, and its output was measured with a thermal-conductivity detector. The nitrogen was assumed to have originated from air inleakage, and a correction was made for the corresponding amount of argon in air. This correction never exceeded 1%.

RESULTS

The procedures described above were followed in most experiments. To establish that these procedures led to valid results, variations were made in the preliminary experiments; e.g., the time of bubbling was varied from 1/2 to 3 hr, the rate of bubbling was varied from 1/2 to 1 liter/min, the quiescent period was extended from overnight to several days, and multiple stripping was attempted. From the results of these preliminary runs, we concluded that, with respect to the time element, the selected procedures led to the required degree of saturation and stripping.

The experimental isothermal pressure dependence of solubility was determined from 14 measurements at ~500°C for helium and from eight measurements at ~480°C for argon. The results are shown in Figs. 2 and 3, where the mole fractions of helium (corrected to exactly 500°C) and of argon (corrected to exactly 480°C) are plotted against the gas pressure. The corrections were based on the measured isobaric temperature coefficients of solubility determined in this work. The experimental points were fitted by the method of least squares to unconstrained linear equations. On the basis of statistical F-tests, the displacements of the lines from the origins and their deviations from linearity were found to be insignificant. This can be seen in Figs. 2 and 3 by the position of the 95% confidence limits. The solubility data, therefore, obey Henry's law to at least 9 atm pressure.

The solubilities of helium and argon were measured at approximately 50°C intervals between 330 and 550°C with at least quadruplicate determinations at each temperature. The temperatures are believed to be accurate to within 1°.

Gas solubilities are conventionally expressed in terms of two different units (a general review of these units appears in Ref. 12): (1) Henry's-law constant, K_H, atom fraction of solute in solution per atmosphere of gas pressure; and (2) Ostwald coefficient, $\lambda = C_\ell/C_g$, the ratio of the concentration of the solute in the liquid phase to the concentration of the solute in the gaseous phase in equilibrium with it. Thus, the Ostwald coefficient may be regarded as a partition coefficient of the solute, one phase being a gas and the other a liquid. When the gaseous phase is pure and ideal, the units K_H and λ are related to each other by the equation $\lambda = R'TdK_H/M$, where $R' = 82.06$ cm³-atm/deg-mol is the gas constant, T is the Kelvin temperature, d is the density of the solvent, and M its molecular weight. (For liquid sodium[13] $d(\mathrm{g/cm^3} = 0.950 - 2.30 \times 10^{-4}t - 1.46 \times 10^{-8}t^2 + 5.64 \times 10^{-12}t^3$, where t is the temperature in °C, and M = 22.99 g/mol.) Heats of solution may be calculated from the temperature coefficients of solubility by the relations

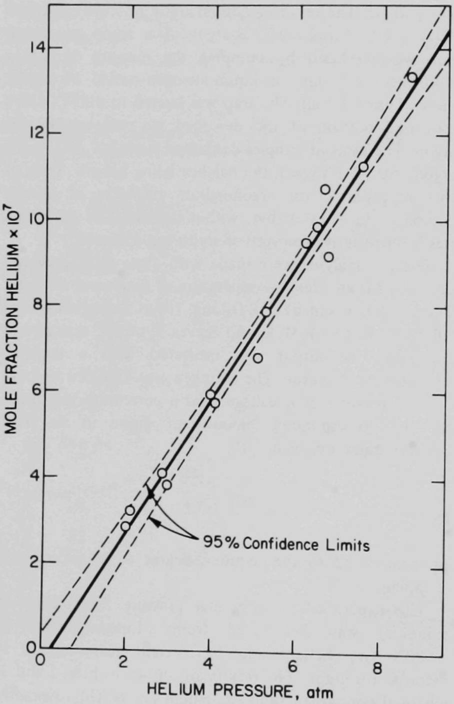

Fig. 2. Pressure Dependence of the Solubility of Helium in Sodium at 500°C. ANL Neg. No. 308-2320.

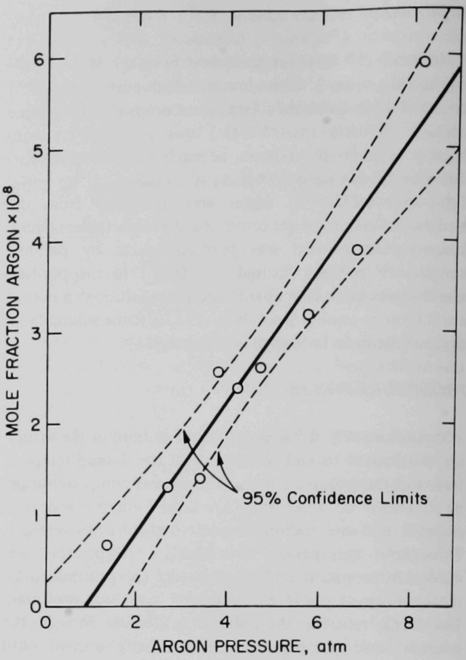

Fig. 3. Pressure Dependence of the Solubility of Argon in Sodium at 480°C. ANL Neg. No. 308-2321.

$$\bar{H}_2(\mathrm{soln},T,P) - H_2^\circ(g,T,P = 1\ \mathrm{atm}) = -R[\partial \ln K_H/\partial(1/T)] \quad (1)$$

and

$$\bar{H}_2(\mathrm{soln},T,P) - H_2^\circ(g,T,P = R'Td/M) = -R[\partial \ln \lambda/\partial(1/T)]\ .(2)$$

The heats of solution defined in Eqs. 1 and 2 differ from each other with respect to the choice of the standard state of the solute. The standard state used in Eq. 1 is one gram-atom of ideal gas at temperature T and a pressure of 1 atm; that used in Eq. 2 is one gram-atom of ideal gas at temperature T in a volume equal to the molar volume of solvent.

HELIUM

The results of 30 determinations for the solubility of helium in sodium are shown in Table I and in Fig. 4. Over the range 350–550°C, the data were fitted by the following equations:*

$$\log K_H = -3.16 - 2833T^{-1} \qquad (3a)$$

or

$$\log \lambda = 0.516 - 3078T^{-1} \qquad (3a)$$

A statistical analysis showed that a mean result of a prolonged series of measurements would be predicted by Eq. 3 with an uncertainty (95% confidence level) of less than 4%. For the standard state defined as one gram-atom of ideal gas at 1 atm, the heat of solution is 13.0 ± 0.4 kcal/mol; for the standard state defined as one gram-atom of ideal gas in a volume equal to the molar volume of sodium, the heat of solution is 14.1 ± 0.6 kcal/mol.

The helium solubility line reported by Thormeier [9] is also shown in Fig. 4.* At higher temperatures, the two studies agree within experimental error. At lower temperatures, however, the results diverge. The disagreement is reflected in the heats of solution; 16.4 kcal/mol, reported by Thormeier, is well outside the error limits assigned to the presently reported heat, 13.0 ± 0.4 kcal/mol. The main differences between our procedure and Thormeier's appear to be in the manner of equilibrating the saturating gas with the liquid and the manner of stripping and analyzing the dissolved gas. Thormeier pumped liquid sodium into a tank containing the saturating gas, instead of bubbling the saturating gas through the sodium. For stripping, Thormeier used evacuation rather than sparging, and the quantity of recovered gas was determined in a volumeter without compositional analysis. In the light of these differences and in the absence of an error or reproducibility analysis by

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*For technical purposes, the solubility of natural helium expressed in weight units is given by log (ppb/atm He) = 5.09 - 5099T^{-1}, where T is in degrees Rankine.

*Solubility results reported in Ref. 9 are expressed in units of a technical atmosphere, ata. This unit is equal to a pressure of 1 kg/cm^2. The appropriate conversion factor is 1 atm = 1.0333 ata.

TABLE I. Dependence of the Solubility of Helium in Liquid Sodium on Temperature and Pressure

Temperature, °C	Pressure, P, atm	Solubility, x, atom fraction x 10^7	Henry's Law Constant, x/P, atm^{-1} x 10^8	Ostwald Coefficient, x 10^5
551.6	6.60	17.6	26.7	64.4
552.0	6.47	15.0	23.2	56.0
550.1	6.95	18.6	26.8	64.5
548.0	6.54	17.3	26.5	63.8
500.0	1.97	2.86	14.5	33.2
500.8	2.08	3.22	15.5	35.5
499.2	2.82	4.12	14.6	33.4
497.8	2.95	3.84	13.0	29.6
499.2	3.93	5.93	15.1	34.6
498.2	4.02	5.63	14.0	32.1
501.9	5.04	6.96	13.8	31.8
506.2	5.23	8.42	16.1	37.3
498.0	6.16	9.30	15.1	34.5
500.4	6.43	9.90	15.4	35.3
494.9	6.59	10.1	15.4	35.1
497.4	6.70	8.91	13.3	30.4
500.8	7.50	11.3	15.1	34.8
501.3	8.61	13.5	15.7	36.2
445.8	6.21	5.11	8.23	17.8
447.0	6.40	5.32	8.31	18.0
447.3	6.57	5.96	9.07	19.7
450.6	6.64	4.85	7.31	15.9
402.6	6.73	3.24	4.81	9.91
401.0	6.59	2.90	4.40	9.06
399.8	6.77	2.92	4.32	8.87
400.0	6.56	2.37	3.61	7.42
348.2	6.84	1.25	1.83	3.52
352.1	6.75	1.39	2.06	4.00
348.8	6.85	1.43	2.09	4.03
349.0	6.74	1.27	1.89	3.64

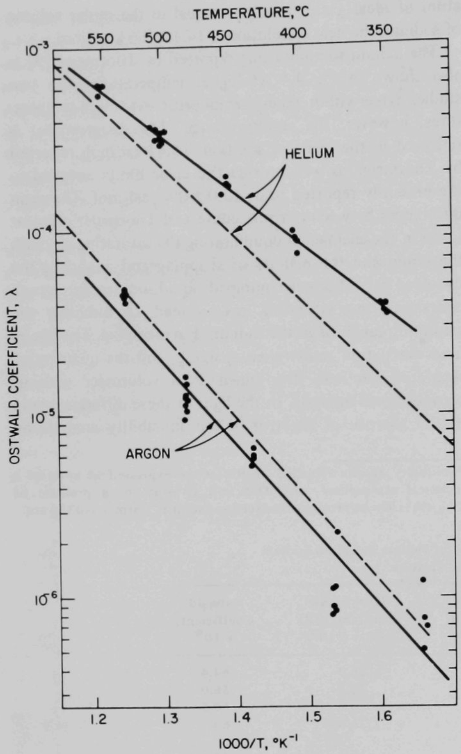

Fig. 4. Temperature Dependence of the Solubility of Helium and Argon in Sodium: ——●——, this work; — — — — — —, Thormeier [9]. ANL Neg. No. 308-2318.

Thormeier, it is difficult to comment further on the source of discrepancy.

ARGON

The results for argon are shown in Table II and Fig. 4. Over the range 330–530°C, the solubility data (30 points) were well fitted to linear equations* by the method of least squares:

$$\log K_H = -2.59 - 4221T^{-1} \tag{4a}$$

or

$$\log \lambda = 1.08 - 4462T^{-1}. \tag{4b}$$

The 95% confidence limits of the predicted mean values of K_H or λ calculated from Eq. 4 are ±16%. Owing to the difficulty of assaying gas mixtures containing less than 5 mol % argon, the reproducibility of the argon results was noticeably inferior to that of the helium results.

The heat of solution of argon in sodium is 19.3 ± 1.2 kcal/mol when the standard state of argon is taken as one gram-atom of ideal gas at 1 atm, or 20.4 ± 2.1 kcal/mol when the standard state corresponds to one gram-atom of ideal gas in a volume equal to the molar volume of sodium.

Thormeier's results for the solubility of argon in sodium [9] are also shown in Fig. 4. The 16% relative uncertainty we have assigned to our results overlaps Thormeier's solubility line at all temperatures, and his reported heat of solution, 20.0 kcal/mol, agrees well with the value 19.3 ± 2.1 kcal/mol from this work.

TABLE II. Dependence of the Solubility of Argon in Liquid Sodium on Temperature and Pressure

Temperature, °C	Pressure, P, atm	Solubility, x, atom fraction × 10^8	Henry's Law Constant, x/P, atm^{-1} × 10^9	Ostwald Coefficient, × 10^6
530.0	3.54	7.01	19.8	46.8
530.5	3.78	7.41	19.6	46.3
530.8	3.91	7.35	18.8	44.5
530.6	6.77	13.8	20.4	48.2
530.2	6.79	13.6	20.0	47.3
529.6	6.80	12.0	17.7	41.8
480.6	1.36	0.677	4.98	11.2
479.6	2.72	1.29	4.74	10.7
480.4	3.40	1.41	4.15	9.33
478.4	3.78	2.49	6.59	14.8
480.2	4.22	2.39	5.66	12.7
479.6	4.71	2.58	5.48	12.3
479.6	5.74	3.17	5.52	12.4
479.8	6.80	3.77	5.54	12.5
479.6	8.19	5.88	7.18	16.1
430.1	6.73	1.80	2.67	5.68
430.6	6.78	2.10	3.10	6.60
431.0	6.80	1.65	2.43	5.18
430.7	6.81	1.94	2.85	6.07
379.8	6.76	0.295	0.436	0.874
380.4	6.80	0.374	0.550	1.10
379.0	6.82	0.282	0.413	0.827
379.0	6.84	0.383	0.560	1.12
380.4	6.84	0.271	0.396	0.794
377.2	6.87	0.769	1.12	2.24
330.2	6.67	0.268	0.402	0.755
331.0	6.70	0.435	0.649	1.22
330.4	6.77	0.186	0.275	0.517
328.8	6.80	0.250	0.368	0.690
329.0	6.83	0.251	0.367	0.688

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*For technical purposes, the solubility of argon expressed in weight units is given by log (ppb/atm Ar) = 6.65 - 7598T^{-1}, where T is in degrees Rankine.

DISCUSSION

THERMODYNAMIC APPROACH

The solubility of noble gases in liquid metals may be examined on the basis of theoretical models. Consider a binary system composed of two phases: a dilute solution of a noble element (2) in a solvent (1), and gaseous phase containing only the noble element. At equilibrium, the chemical potential of the noble element will be the same in both phases:

$$\mu_2(\mathrm{sol,T,P}) = \mu_2(\mathrm{g,T,P}). \tag{5}$$

For the chemical potential of the noble element in the solution, one may write

$$\mu_2(\mathrm{sol,T,P}) = \mathrm{R'T} \ln (x_2 \gamma_2) + \mu_2^\circ(\ell,\mathrm{T,P}), \tag{6}$$

where x_2 is the mole fraction, γ_2 is the activity coefficient of the solute, and the superscript ° refers to a standard state consisting of the pure, liquid noble element at temperature T and pressure P. (Above the critical temperature, this standard state is a hypothetical one.) For the gas phase at the same temperature and pressure,

$$\mu_2(\mathrm{g,T,P}) = \mathrm{R'T} \ln \mathrm{P} + \beta \mathrm{P} + \mu_2^\circ(\mathrm{g,T,1\ atm}). \tag{7}$$

In Eq. 7, the virial series has been terminated at β, the second virial coefficient of the gas. The chemical potential of the pure, liquid noble element under its own vapor pressure, P_2°, may be written as

$$\mu_2^\circ(\ell,\mathrm{T},P_2^\circ) = \mathrm{R'T} \ln P_2^\circ + \beta P_2^\circ + \mu_2^\circ(\mathrm{g,T,1\ atm}). \tag{8}$$

Combination and rearrangement of Eqs. 5–8 yield

$$\ln K_H \equiv \ln (x_2/\mathrm{P}) = -\ln P_2^\circ + (\mathrm{P} - P_2^\circ)(\beta - V_2^\circ)/\mathrm{R'T} - \ln \gamma_2 \tag{9a}$$

or

$$\ln \lambda = \ln (\mathrm{R'T}/P_2^\circ V_1) + (\mathrm{P} - P_2^\circ)(\beta - V_2^\circ)/\mathrm{R'T} - \ln \gamma_2. \tag{9b}$$

In Eq. 9, $\mu_2^\circ(\ell,\mathrm{T},P_2^\circ) - \mu_2^\circ(\ell,\mathrm{T,P})$ was taken to be equal to $V_2^\circ(P_2^\circ - \mathrm{P})$, where V_2° is the molar volume of the pure, liquid noble element.

One method of estimating the activity coefficient of the solute is through the use of Hildebrand's solubility parameters [14]:

$$\ln \gamma_2 = \ln (V_2^\circ/V_1) + (1 - V_2^\circ/V_1) + V_2^\circ(\delta_2 - \delta_1)^2/\mathrm{RT}. \tag{10}$$

With this estimate,

$$\ln \lambda = \ln (\mathrm{R'T}/P_2^\circ V_2^\circ) - V_2^\circ(\delta_2 - \delta_1)^2/\mathrm{RT} + (\mathrm{P} - P_2^\circ)(\beta - V_2^\circ)\mathrm{R'T} - (1 - V_2^\circ/V_1). \tag{11}$$

This method of estimation was used by Epstein [1] for helium in sodium and by Mitra [4] for xenon in bismuth. Epstein's predicted value at 482°C, $K_H = 1.5 \times 10^{-10}$ atm^{-1}, is lower than our measured solubility by a factor of 10^3. Mitra's value at 500°C, $K_H = 1.3 \times 10^{-10}$ atm^{-1}, does not disagree with the best experimental result[5], $<2 \times 10^{-10}$ atm^{-1}.

STATISTICAL–MECHANICAL APPROACH

The problem may also be examined by considering the statistical mechanics of the interaction between the solvent and the solute atoms, the latter being treated as a quasi-gas moving freely in the volume occupied by the solution. Under these conditions, the molar chemical potential of the solute may be expressed by the equation (see Ref. 15, p. 373)

$$\mu_2(\mathrm{sol,T,P}) = -N_0 \chi_2 + \mathrm{P}\overline{V}_2 - \mathrm{RT} \ln \phi_2(\mathrm{T}) + \mathrm{RT} \ln C_{\mathrm{sol}}, \tag{12}$$

where χ_2 is the molecular potential energy of a solute atom, relative to the state of infinite separation, $\overline{V}_2$ is the partial molar volume of the solute, $\phi_2(\mathrm{T})$ is the partition function of the solute, including both translational and internal degrees of freedom, and C_{sol} is the concentration of solute atoms in solution.

Similarly, for the gaseous phase, the molar chemical potential may be written as

$$\mu_2(\mathrm{g,T,P}) = -\mathrm{RT} \ln \phi_2(\mathrm{T}) + \mathrm{RT} \ln C_g, \tag{13}$$

where C_g is the concentration of noble element atoms and it is assumed that the translational and internal degrees of freedom of the solute are unaffected by the solution process.

Equations 5, 12, and 13 may be combined to yield

$$\mathrm{RT} \ln \lambda \equiv \mathrm{RT} \ln (C_{\mathrm{sol}}/C_g) = N_0 \chi_2 - \mathrm{P}\overline{V}_2. \tag{14}$$

The quantity $(-N_0\chi_2 + \mathrm{P}\overline{V}_2)$ represents the reversible work of adding one mole of noble gas to the pure solvent to form an infinitely dilute solution. For solution of gases in liquids, Uhlig [16] proposed an atomistic model which is equivalent to replacement of the quantity $(-N_0\chi_2 + \mathrm{P}\overline{V}_2)$ by the sum of two terms: μ_c, the reversible work required to make a mole of internal cavities, of a size corresponding to the molar volume of the solute, in the body of the solvent; and μ_i, the reversible work corresponding to the interaction of the solute atoms with the surrounding solvent. Several methods have been proposed for evaluating these terms. Uhlig considered μ_c to be equal to the work done to make internal surfaces against the solvent's macroscopic surface tension; he did not attempt to evaluate the interaction term independently. McMillan [2] estimated the energy of cavity formation to be the product of the surface area of the cavity and a microscopic surface energy. The latter was estimated as one-fourth of the energy of vaporization per unit area occupied by solvent atoms in the normal surface. The energy of interaction was calculated with the London equation for the dispersion forces between the solute atom and only the nearest-neighbor solvent atoms. Johnson and Shuttleworth [6] proposed a model similar to Uhlig's, except that the translational modes of the solute atoms are supplemented by vibrational ones; i.e., $(-N_0\chi_2 + P\overline{V}_2) = \mu_c + \mu_i + \mu_{vib}$. They considered μ_c to be given by the surface area of a solute atom multiplied by the surface energy of the solvent, approximated (by a comparison with surface adsorption potentials) μ_i to be constant at -5 kcal/mol, and estimated the vibrational contribution, $\mu_{vib} = H_{vib} - TS_{vib}$, of the solute by taking H_{vib} and S_{vib} to be equal to the enthalpy and entropy of the solvent. In addition, Johnson and Shuttleworth did not assign equal values to the partition function of component 2 in the gaseous and in the solution phases (see Eqs. 12 and 13). Instead, for the gas, the partition function was represented by its translational component, $(2\pi mkT)^{3/2}/h^3$, and, for the solution phase, by the number density of the solvent. Using the Johnson and Shuttleworth approach, Slotnick *et al.* [8] found the predicted solubilities of helium in liquid lithium and potassium to be about 600 times larger than the experimental results. Pierotti [17], in a more sophisticated treatment, evaluated μ_c as the free energy of cavity formation in a hard-sphere fluid, using methods developed by Reiss *et al.* [18]. The interaction term, μ_i, was evaluated in terms of an integrated form of the Lennard-Jones (12–6) potential with the Kirkwood-Muller equation for the dispersion forces.

TEST OF EXISTING MODELS

All the models capable of quantitative evaluation were tested against the solubilities of helium and argon in liquid sodium. The results are shown in Table III.

1. In the Epstein model, the predicted solubility depends markedly on the value assigned to the hypothetical quantity P_2°. Values of P_2° were obtained by extrapolation of the vapor-pressure equations from the accessible regions to the supercritical regions. These equations were as follows:

$$\text{Helium [19]}: \log P_2^\circ\ (\text{atm}) = 1.848 - 7.948T^{-1} - 0.1363T^{-2} + 4.363T^{-3};$$

$$\text{Argon [20]}: \log P_2^\circ\ (\text{atm}) = 3.964 - 346T^{-1}.$$

For this model, the molar volumes, $V_{He}^\circ = 31.8$ cm^3 and $V_{Ar}^\circ = 24.2$ cm^3, were taken unchanged from their values at the normal boiling points. Hildebrand's solubility parameters ($\delta_{He} = 0.588$ cal$^{1/2}$ cm$^{-3/2}$, $\delta_{Ar} = 7.56$ cal$^{1/2}$ cm$^{-3/2}$, $\delta_{Na} = 27.50$ cal$^{1/2}$ cm$^{-3/2}$) were estimated (see Ref. 15, p. 424) from the heats of vaporization at the normal boiling points. The second virial coefficients were taken to be 10.76 cm^3/mol (300°C) and 10.14 cm^3/mol (500°C) for helium [21] and 10.77 cm^3/mol (300°C) and 17.76 cm^3/mol (500°C) for argon [22].

2. In McMillan's model, the interaction term was calculated from

$$\mu_i = -Z(3/2)(\alpha_1\alpha_2/a_{12}^6)[I_1I_2/(I_1 + I_2)],$$

where α is the atomic polarizability (α_{He} [23] = 0.204×10^{-24} cm^3, α_{Ar} [23] = 1.63×10^{-24} cm^3, α_{Na} [23] = 29.7×10^{-24} cm^3), I is the ionization potential (I_{He} [24] = 24.581 eV, I_{Ar} [24] = 15.756 eV, I_{Na} [24] = 5.138 eV), a_{12} is the distance between the centers of the solute and solvent atoms ($a_{Na\text{-}He} \cong 3.21 \times 10^{-8}$ cm, $a_{Na\text{-}Ar} \cong 3.60 \times 10^{-8}$ cm), and Z is the number of nearest sodium neighbors, estimated to be 9.4 and 11.8 for helium and argon, respectively. The cavity term, μ_c, was calculated from $\mu_c = \pi a_{12}^2 \Delta H_1^V / 4N_0\sigma$, where ΔH_1^V is the heat of vaporization of sodium (23.7 kcal/mol) and σ is the cross-sectional area of a solvent atom on the surface ($\sigma_{Na} \cong 24.8 \times 10^{-16}$ cm^2).

3. In Johnson and Shuttleworth's model, the cavity term was calculated from $\mu_c = 4\pi a_2^2 \gamma_1^\circ$, where a_2 is the radius of the solute atom ($a_{He} \cong 1.32 \times 10^{-8}$ cm, $a_{Ar} \cong 1.70 \times 10^{-8}$ cm) and γ_1° is the hypothetical surface energy of liquid sodium at 0°K (220 erg/cm^2) [25]. For the calculation of the vibrational term, the enthalpy and entropy of

TABLE III. Ostwald Coefficients for Solution of Helium and Argon in Liquid Sodium at 300 and 500°C

Model	Na-He		Na-Ar	
	300°C	500°C	300°C	500°C
Epstein [1]	4.56×10^{-8}	1.06×10^{-5}	3.23×10^{-4}	1.90×10^{-3}
McMillan [2]	0.86	0.89	>1	>1
Johnson and Shuttleworth [6]	6.47×10^{-2}	1.79×10^{-1}	3.72×10^{-5}	2.90×10^{-4}
Pierotti [17]	1.26×10^{-2}	2.78×10^{-2}	5.24×10^{-3}	1.25×10^{-2}
Observed (this work)	1.36×10^{-6}	3.24×10^{-4}	1.98×10^{-7}	2.04×10^{-5}

sodium [26] were taken to be 4.16 kcal/mol and 18.7 cal/deg-mol for 300°C and 5.57 kcal/mol and 20.8 cal/deg-mol for 500°C, respectively.

4. The reader is referred to Pierotti's paper [17] for details of his model. Here, the calculated solubility is a sensitive function of the value selected for the hard-sphere diameter of the solvent. We have selected 3.19 Å for 300°C and 3.12 Å for 500°C as the hard-sphere diameter of sodium, as discussed by Ascarelli [27]. The values for the atomic magnetic susceptibilities [23] required for the calculation of the Kirkwood-Muller interaction term were taken to be $\chi_{He} = -2.90 \times 10^{-30}$ cm³, $\chi_{Ar} = -3.24 \times 10^{-29}$ cm³, and $\chi_{Na} = -9.00 \times 10^{-29}$ cm³.

CONCLUSION

Examination of Table III shows that Epstein's model predicts solubilities much larger and much smaller than those observed. A major weakness of this model is the need for extrapolation of the vapor pressure of the solute to unphysical regions. For helium, in particular, the quantum effects which dominate the vapor pressure of the liquid at low temperatures would be poorly taken into account by simple extrapolation to higher temperatures. The models proposed by McMillan, by Johnson and Shuttleworth, and by Pierotti yield solubilities generally higher than those observed. It is suggested that the inadequacies of these models stem primarily from their estimates of the cavity-formation term. These estimates, which may be adequate for insulating solvents, seem to fail for metallic solvents. A theoretical treatment which specifically deals with the electronic work of cavity formation in a metallic solvent seems required. Such a model has been developed in this laboratory and will appear elsewhere [28].

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